Synthesis and Characterization of a Novel Polymeric System Bearing a Benzophenone Borate Salt as a New Photoinitiator for UV Curing[1]

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ABSTRACT: Polymeric photoinitiators bearing benzophenone triphenylbutyl borate salt as the side chain have been synthesized and characterized and their activity measured in the photoinitiated polymerization of a bifunctional monomer, diethylene glycol diacrylate. The results were compared with a low-molecular weight model compound. At lower concentrations of the requisite benzophenone moiety, the highest activity was observed for the model compound, while at higher concentrations the homopolymer was superior. For both cases, the lowest photoinitiation activity was observed with significant induction period for copolymers with methyl methacrylate when compared to the homopolymer. The results are discussed in light of the microenvironment of the initiator fragments in the polymeric systems.

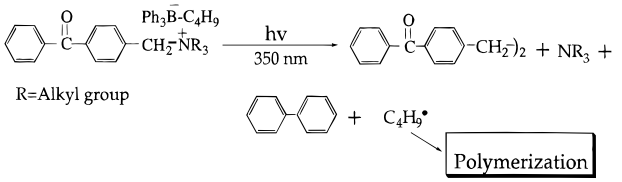
Introduction

Polymeric materials bearing photosensitive groups either in the backbone or side chain have recently been of growing interest as photoinitiators.[2,3] Polymeric photoinitiators have several advantages when compared to conventional photoinitiators with respect to their stability under daylight exposure, odor due to formation of volatile components, and toxicity. In some cases,[4−6] a higher photoinitiation capability was observed for polymeric systems when compared to low-molecular weight analogues. In principle, properly designed polymeric systems containing photoactive groups should show a higher activity due to the microenvironment of the polymer chain cage which should reduce the tendency toward nonproductive radical coupling processes.

Recently, we have reported a new class of novel photointiators *N*,*N*,*N*-trialkyl-*N*-(*p*-benzoyl)benzyl ammonium triphenylbutylborates.[7] These produce upon irradiation a butyl radical from the borate counterion which initiates the free radical polymerization of acrylic or vinylic monomers efficiently. The formation of the butyl radical proceeds via electron transfer to the excited benzophenone triplet state from the boronyl anion. Subsequent rearrangement and bond cleavage generates the products as shown in Scheme 1. These findings clearly indicate that polymers bearing the benzophenone triphenylbutyl borate group, if properly designed and synthesized, could improve the performance in photoinitiated polymerization due to the macromolecular nature of the system.

In this paper we report the synthesis and characterization of polymeric photoinitiators bearing benzophenone borate salts as the side chain. Their photoactivities in the polymerization of acrylate monomers were evaluated and compared with a low-molecular weight model compound synthesized and characterized separately. The photoinitiating process will be discussed in terms of photoinduced intra- and intermolecular electron transfer mechanism.

Scheme 1



Experimental Section

General. Melting point determinations were made using a Thomas Hoover capillary melting point apparatus; all temperatures are uncorrected. All compounds were characterized by NMR, IR, and elemental analysis, which was performed by Atlantic Microlab, Inc., Georgia. Nuclear magnetic resonance (NMR) spectra was taken on Gemini GEM-200 (200 MHz) and Varian Unity+ 400 (400 MHz) spectrometers. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) at 0.0 ppm on the δ scale. ^{11}B spectra were recorded on a Varian Unity+ 400 (128 MHz) spectrometer with $B(OMe)_3$ as the external standard. IR spectra were obtained on a 6020 Galaxy FTIR spectrometer.

Thermogravimetric analysis (TGA) was carried out on a DuPont TGA-951 interfaced with a thermal analyzer 2100 system. TGA samples were heated at a rate of 20 °C/min with a purified N_2 gas flow of 20 cm^3/min. TGA was used to characterize polymers with respect to composition, degree of weight loss, and decomposition temperature. Phase transition temperatures were measured with a DuPont 990 thermal analyzer coupled to a 910 differential scanning calorimeter (DSC). The calorimeter was calibrated with indium and tin under a nitrogen flow with both the heating and cooling rates of 10 °C/min. The peak maxima of the endotherms were taken as the transition temperatures.

Photoinitiating Activity Measurement. A calculated amount of photoinitiator was added to the bifunctional acrylic monomer, diethylene glycol diacrylate, and the mixture was stirred for several hours to form a homogenous solution. (In some cases we needed to stir at 60 °C.) A few drops of the formed solution were placed between regular NaCl plates using a 15 μm thick Teflon spacer and cured using a high-pressure Hg arc lamp (200 W) as the light source. A cutoff filter that allowed only the narrow band at 365 nm to penetrate the sample was used. Double bond conversion (acrylate to polyacrylate) was monitored by observing the disappearance of the absorption peak at 810 cm^{-1} due to the C=C of acrylate[8] in the FTIR according to the following formula.

$$\mathrm{DC} = (X_0 - X_i/X_0) \times 100\%, \quad \text{where } X = A\ (810\ \mathrm{cm}^{-1})$$

Synthesis. (a) 2-(Dimethylamino)ethyl Isobutyrate (2). To a solution of *N*,*N*-dimethyl ethanolamine (4.45 g, 0.05 mol) in 140 mL of anhydrous tetrahydrofuran (THF) at room

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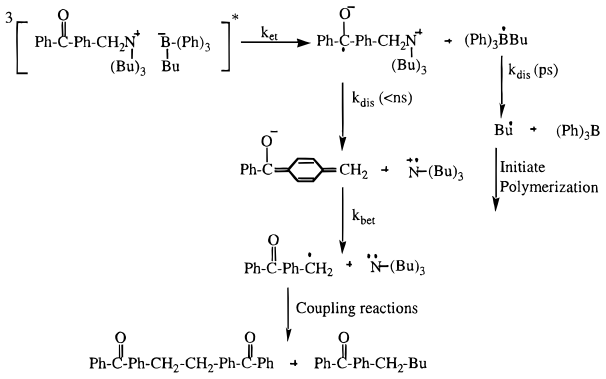
temperature under nitrogen was added triethylamine (5.05 g, 0.05 mol) and stirred for 15 min. The reaction mixture was then cooled at 0 °C, and isobutyryl chloride (5.5 g, 0.05 mol) in 10 mL of tetrahydrofuran was added dropwise over 20 min. The resulting suspension was allowed to warm to room temperature and stirred overnight. The resulting solution was filtered and the solvent evaporated. The resulting product was then diluted by adding 200 mL of ether and subsequently washed with 10% aqueous NaOH solution, water, and brine. After removal of the solvent, the crude product was chromatographed on a silica gel column using chloroform as the eluent to give liquid product **2** (1.44 g, 50%). ^{1}H NMR ($CDCl_3$): δ 4.10 (t, J = 5.82 Hz, O−CH_2−, 2H), 2.50 (m, N−CH_2 and CH(CH_3)$_2$, 3H), 2.21 (s, N−CH_3, 6H), 1.10 (d, CH(CH_3)$_2$, 6H). MS m/z: 159 (M^+), 115, 71, 58 (100%), 42.

(b) *N,N*-Dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl Isobutyrate Ammonium Bromide (3). A solution of **2** (1.85 g, 11.60 mmol), and 4-(bromomethyl)benzophenone[9] (3.18 g, 11.56 mmol) in acetone (50 mL) was stirred at room temperature for 24 h. The solvent was evaporated and the solid product dissolved in a minimum of chloroform. It precipitated when the solution was poured into ether (100 mL). The solid product was filtered, washed with ether, and dried under vacuum. After recrystallization from ethyl acetate/ethanol, **3** was obtained as white needles (3.92 g, 80%); mp 152−4 °C. ^{1}H NMR (CD_3CN): δ 7.80 (m, aromatic protons ortho to C═O, 4H), 7.67 (m, aromatic proton para to C═O, 1H), 7.55 (m, aromatic protons meta to C═O, 4H), 4.98 (s, Ar−CH_2, 2H), 4.58 (br s, O−CH_2, 2H), 3.88 (m, N−CH_2, 2H), 3.21 (s, N−CH_3, 6H), 2.60 (m, CH(CH_3)$_2$, 1H), 1.16 (d, CH(CH_3)$_2$, 6H). Anal. Calcd for $C_{22}H_{28}BrNO_3$: C, 60.86; H, 6.45; N, 3.22. Found: C, 60.62; H, 6.40; N, 3.16.

(c) *N,N*-Dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl Isobutyrate Ammonium Triphenylbutyl Borate (1). Compound **3** (1.0 g, 2.28 mmol) was dissolved in water (10 mL) and filtered. The lithium salt of triphenylbutyl borate (0.66 g, 2.15 mmol) in a minimum of water was added dropwise over 15 min. The solution was then diluted by adding water (75 mL), stirred for 15 min, and filtered. The resulting solid was washed with water several times and dried under vacuum. Compound **1** was obtained as a white powder (1.18 g, 85%); mp 110−1 °C (ethyl acetate). ^{1}H NMR (CD_3CN): δ 7.83 (t, J = 8.0 Hz, aromatic protons ortho to C═O, 4H), 7.70 (m, aromatic protons para to C═O, 1H), 7.59 (m, aromatic protons meta to C═O, 4H), 7.26 (m, aromatic protons ortho to B, 6H), 6.96 (t, J = 8.0 Hz, aromatic protons meta to B, 6H), 6.79 (t, J = 6.5 Hz, aromatic protons para to B, 3H), 4.51 (s, CH_2−Ar, 2H), 4.49 (m, O−CH_2, 2H), 3.65 (m, N−CH_2, 2H), 2.94 (s, N−CH_3, 6H), 2.62 (m, CH(CH_3)$_2$, 1H), 1.93 (m, overlap with solvent peak, B−CH_2, 2H), 1.16 (d, CH(CH_3)$_2$, 6H), 0.90 (m, B−CH_2−C_2H_4−, 4H), 0.77 (t, J = 6.5 Hz, B−C_3H_6−CH_3, 3H). Anal. Calcd for $C_{44}H_{52}BNO_3$: C, 80.89; H, 7.96; N, 2.14. Found: C, 80.72; H, 7.93; N, 2.18.

(d) *N,N*-Dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl Methacrylate Ammonium Triphenyl Butyl Borate (4). Tetramethylammonium triphenylbutylborate[10] (1.0 g, 2.68 mmol) was dissolved in 60 mL of hot acetone (50 °C) and the resulting solution filtered. A solution of *N,N*-dimethyl-*N*-(*p*-benzoyl)-benzyl-*N*-ethyl methacrylate ammonium bromide[11] (1.16 g, 2.68 mmol) in a minimum amount of hot acetone (with 1.0 mL of methanol) was added dropwise. The reaction mixture became cloudy (due to formation of tetramethylammonium bromide), but it could be turned into clear solution upon addition of a few milliliters water. After the mixture was stirred for 1h at 45−50 °C, product was precipitated by adding 100 mL of water. The white product was filtered, washed with water several times, and dried under vacuum. Compound **4** was obtained as white semicrystals (1.50 g, 86%); mp 133−134 °C. ^{1}H NMR (CD_3CN): δ 7.83 (m, aromatic protons ortho to C═O, 4H), 7.59 (m, aromatic protons meta and para to C═O, 5H), 7.26 (m, aromatic protons ortho to B, 6H), 6.96 (m, aromatic protons meta to B, 6H), 6.83 (m, aromatic protons para to B, 3H), 6.14 (s, C═CH_2, 1H), 5.74 (s, C═CH_2, 1H), 4.53 (br s, CH_2−Ph, 2H), 4.46(s, −O−CH_2, 2H), 3.58 (m, N−CH_2, 2H), 2.95 (s, N−CH_3, 6H), 1.94 (s, ═C−CH_3, 3H), 1.23 (m, B−CH_2, 2H), 0.91 (m, B−CH_2−C_2H_4, 4H), 0.77 (t, J = 7.0 Hz, B−C_3H_6−CH_3, 3H). ^{11}B NMR (DMSO): δ −28.52. Anal. Calcd for $C_{44}H_{50}BNO_3$: C, 81.14; H, 7.68; N, 2.15. Found: C, 81.06; H, 7.68; N, 2.12.

Scheme 2



Typical Procedure for Radical Polymerization. A solution containing the desired amount of monomer or monomers in anhydrous acetonitrile and 2,2′-azobis(isobutyronitrile), AIBN (3 mol % of total monomers), were charged into an oven-dry polymerization tube. The polymerization tube was subjected to four freeze−pump−thaw cycles, sealed, and heated at 60 °C for 120 h. The resulting reaction mixture was poured dropwise into a 20-fold excess diethyl ether. The polymer was collected by filtration and purified by reprecipitation from acetonitrile in diethyl ether and methanol for homo- and copolymers, respectively.

H1. 70% yield by weight. ^{1}H NMR (CD_3CN): δ 7.38−7.80 (br m, 9H, benzophenone moiety), 7.28 (m, aromatic protons ortho to B, 6H), 6.95 (m, aromatic protons meta to B, 6H), 6.78 (m, aromatic protons para to B, 3H), 4.39 (br, Ph−CH_2, 2H), 3.39 (m, O−CH_2, 2H), 2.88 (br, CH_2−N, 2H), 2.16 (s, N−CH_3, 6H), 1.93 (m, α-methyl, 3H), 1.16 (m, B−CH_2, 2H), 0.90 (m, B−CH_2−C_2H_4−, 4H), 0.73 (t, J = 7.0 Hz, B−C_3H_6−CH_3, 3H). Anal. Calcd for $C_{44}H_{50}BNO_3$: C, 81.14; H, 7.68; N, 2.15. Found: C, 80.45; H, 7.60; N, 2.51.

CP1. 76% yield by weight. ^{1}H NMR (CD_3CN): δ 7.40−7.88 (m, 9H, benzophenone moiety), 7.30 (m, aromatic protons ortho to B, 6H), 6.92 (m, aromatic protons meta to B, 6H), 6.86 (m, aromatic protons para to B, 3H), 4.22 (br, Ph−CH_2, 2H), 3.40−3.50 (br, O−CH_2 and O−CH_3, 5H), 2.70 (br, CH_2−N, 2H), 2.14 (s, N−CH_3, 6H), 1.94 (m, 6H, two α-methyl), 1.20 (m, B−CH_2, 2H), 0.92 (m, B−CH_2−C_2H_4, 4H), 0.78 (t, J = 7.0 Hz, B−C_3H_6−CH_3, 3H). Anal. Calcd for $(C_{44}H_{50}BNO_3)_{0.50}$-$(C_5H_8O_2)_{0.50}$: C, 78.33; H, 7.72; N, 1.86. Found: C, 77.54; H, 7.76; N, 1.78.

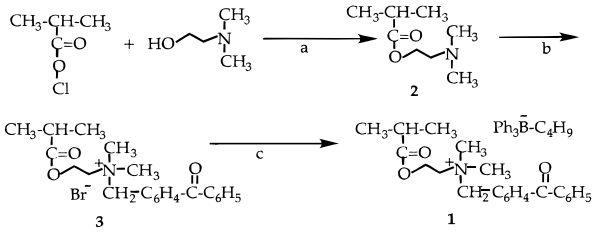
CP2. 73% yield by weight. ^{1}H NMR (CD_3CN): δ 7.45−7.95 (m, 9H, benzophenone moiety), 7.28 (m, aromatic protons ortho to B, 6H), 6.98 (m, aromatic protons meta to B, 6H), 6.82 (m, aromatic protons para to B, 3H), 4.40 (br, Ph−CH_2, 2H), 3.56 (s, O−CH_2 and O−CH_3 of MMA, 5H), 2.90 (br s, N−CH_2, 2H), 2.18 (s, N−CH_3, 6H), 1.98 (m, two α-methyl, 6H), 1.24 (m, B−CH_2, 2H), 0.95 (m, B−CH_2−C_2H_4−, 4H), 0.80 (m, B−C_3H_6−CH_3, 3H). Anal. Calcd for $(C_{44}H_{50}BNO_3)_{0.20}$ $(C_5H_8O_2)_{0.80}$: C, 73.10; H, 7.80; N, 1.33. Found: C, 73.04; H, 7.86; N, 1.4.

Results and Discussion

Design Strategies. In our previous work,[7] we found that *N,N,N*-trialkyl-*N*-(*p*-benzoyl)benzyl ammonium triphenylbutyl borate gives butyl radical upon irradiation at 350 nm, in the typical absorption band of the benzophenone chromophore. Formation of the butyl radical takes place because the benzophenone triplet state oxidizes the borate anion. In a time frame too short to measure, carbon−nitrogen bond cleavage occurs leading to the formation of free tertiary amine, Scheme 2.

Therefore, we proposed that this group (as a side chain in any suitable polymer) would satisfy our re-

Scheme 3



9(a) Triethylamine, THF, room temperature; (b) 4-(bromomethyl)benzophenone, dry acetone, room temperature; (c) lithium salt of triphenylbutyl borate, water, room temperature.

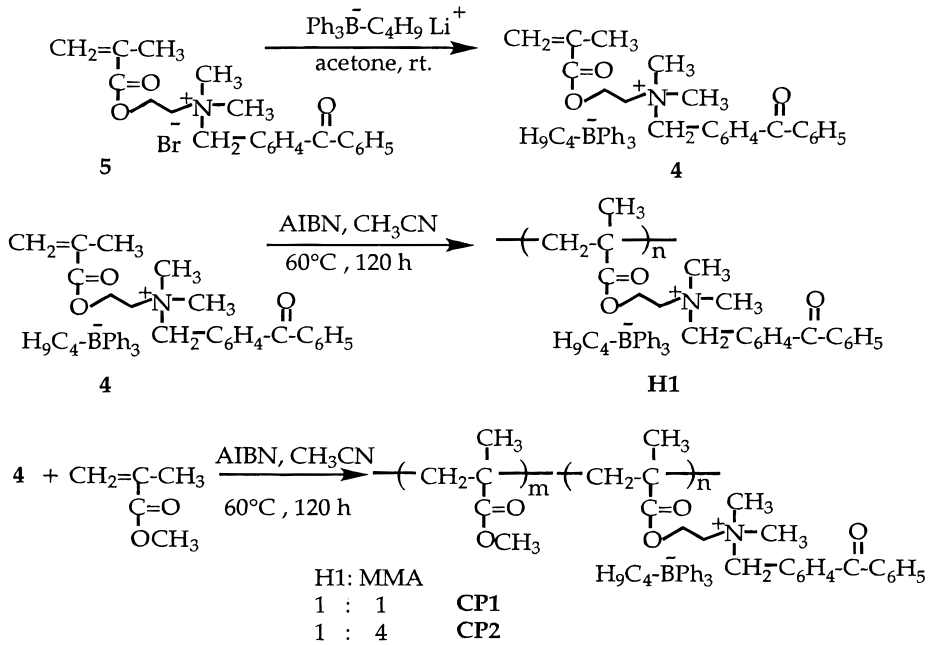
quirements as an active radical generating and transporting species. Moreover, the formation of amine moieties on the photoreactive polymer matrix appears very promising for rapidly curable coatings because of the oxygen scavenging effect of amine functional groups.[12−14] The presence of polymeric amine moieties also has other advantages in terms of improving crosslink density as well as in preventing odors generally associated with volatile amines. In order to incorporate this active species into the polymer chain as a pendant group separated at a definite distance from the backbone, we synthesized a linear, flexible homopolymer. Insertion of an estereal group as a flexible spacer between the benzophenone moiety and the main chain was suggested to improve conformational mobility. This should, therefore, increase the solubility of polymeric initiators in monomers as well as the photoreactivity as a consequence of polymer coiling. We also synthesized copolymers with the conventional comonomer methyl methacrylate in different feed ratios. In this way, the mean sequence length of the benzophenone borate salt units was systematically decreased in the polymeric system by increasing the distance between two side chain benzophenone chromophores. This was anticipated to modulate the initiation activity by controlling the excited state electron transfer reaction in the polymeric environments.

Syntheses of Model Compound and Polymers. Low molecular weight model compound **1** was synthesized in 50% yield, as shown in Scheme 3. Compound **2**, (dimethylamino)ethyl isobutyrate, was obtained by reacting dimethylethanolamine with isobutyryl chloride in the presence of triethylamine in THF solvent with 50% yield. Formation of bromide salt **3**, on the other hand, was accomplished in good yield by reaction with 4-(bromomethyl) benzophenone[9] at room temperature. The exchange of the bromide anion from **3** by triphenylbutyl borate was also a smooth process in water occurring in almost quantitative yield. Monomer **4** was synthesized by modifying our previous reaction sequences.[11] Anion exchange was accomplished from *N*,*N*-dimethyl-*N*-(*p*-benzoyl)benzyl-*N*-ethyl methacrylate ammonium bromide **5** by treatment with tetramethylammonium triphenylbutyl borate in hot acetone and giving analytically pure crystalline **4**.

All polymerization reactions were carried out according to Scheme 4 by free radical polymerization in acetonitrile solvent using AIBN as thermal initiator. The copolymers with methyl methacrylate in the feed ratio 1:1 (**CP1**) and 1:4 (**CP2**) were synthesized at 60 °C in anhydrous acetonitrile for 120 h in a sealed polymerization tube.

Structural Characterization. The ^{1}H NMR spectra of the polymers give some structural information, although most of the peaks were broadened due to long as well as bulky side chains attached to the polymers. However, resonances due to the vinylic moiety in the polymer at about 6.15 and 5.75 ppm were absent. These results indicate no residual monomer to be present in the final polymers (detailed assignments in the Experimental Section). ^{1}H NMR spectra of **H1** showed a broad peak around 3.40 ppm due to the oxymethylene unit, O—CH_2. On increasing the content of the methyl methacrylate (MMA) units in copolymers, the above signals at 3.40 ppm progressively overlapped with the resonances of O—CH_3 of MMA. The multiplicity of the peak at 1.94 ppm was due to α-CH_3 which represents the different tacticity of the polymer backbone. Figure 1 provides a general view of the ^{1}H NMR showing all of the resonances of the homo- and copolymers. On the basis of the signals at 3.40 and 4.22 ppm, the composition of the copolymers was determined[15] (Table 1). FTIR spectra provide additional information about the structure of the polymers. No absorption bands between

Scheme 4



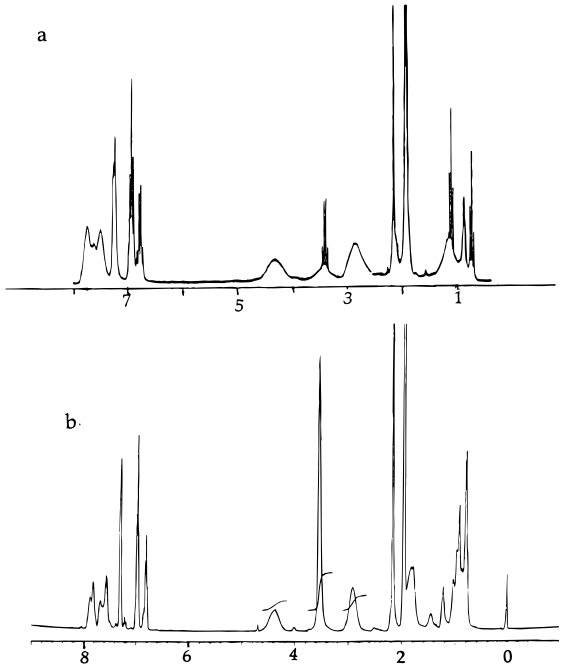


Figure 1. ^{1}H NMR spectra of (a) **H1** and (b) **CP2** in acetonitrile.

Table 1. Synthesis and Feed Compositions of Monomers of Radical Polymerization[a]

sample	feed of BPB (mol %)	conversion[b] (%)	BPB content A[c]	BPB content B[d]
H1	100	70	100	100
CP1	50	76	42.28	44.8
CP2	20	73	18.40	18.9

[a] Heated at 60 °C in CH_3CN with 3 mol % AIBN for 120 h. [b] Calculated as (weight of polymer/weight of monomers) × 100. [c] From carbon and hydrogen analysis data. [d] Calculated from ^{1}H NMR.

1640 and 1620 cm^{-1}, as well as around 1408, 975, and 804 cm^{-1}, typical of the C═C in acrylic groups, were observed. It may be concluded, therefore, that polymerization occurred by involving the acrylic function of both monomers. For all polymers, IR absorptions at 1730 cm^{-1} due to the ester groups of the methacrylate moieties and at 1660 cm^{-1} due to carbonyl on the benzophenone moieties were obvious. The intensities of these two bands reflect the copolymeric composition of the polymers also. In polymer **H1**, where no methyl methacrylate was incorporated, a ratio of the ester/carbonyl of benzophenone (1:1) can be noted (Figure 2). On the other hand, an ester band with an intensity 2× stronger than the carbonyl band appeared in polymer **CP1**. Similarly, the band due to the benzophenone carbonyl in polymer **CP2** was much weaker than that observed in polymer **CP1**. The relative intensity of the absorption at 1150 cm^{-1} due to C—O also changed on composition. These results indicate that the composition of copolymers was basically controlled by the monomer feed ratios.

Quantitative copolymeric composition was determined by elemental analysis. The content of the benzophenone borate unit in the copolymers was estimated by nitrogen analysis. The composition of the monomer units was also calculated from %C and %H analysis data according to eqs 1−4 in which m and n represent the number of moles of BPB and MMA in the copolymers, respectively.

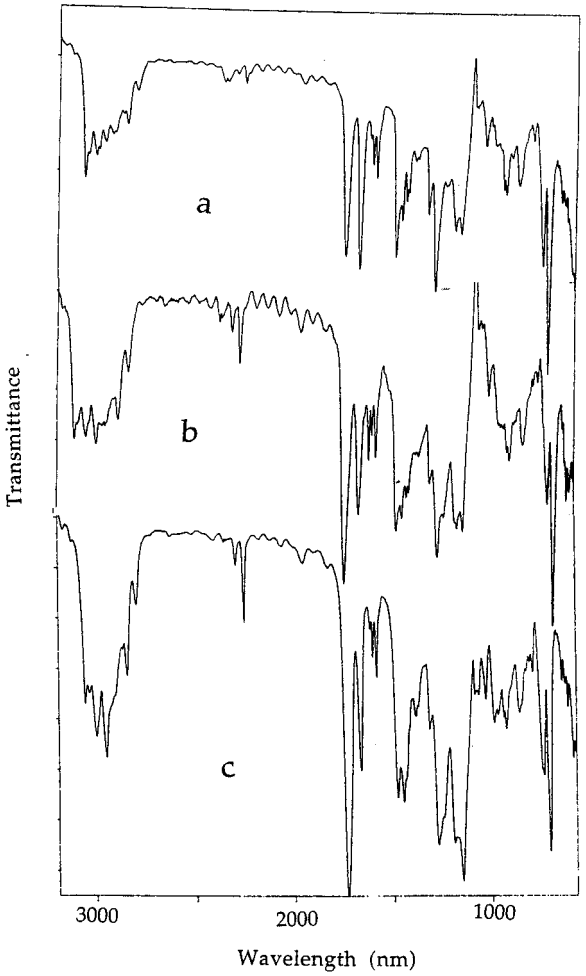


Figure 2. FTIR spectra of (a) **H1**, (b) **CP1**, and (c) **CP2** were taken on thin films cast on a NaCl plate.

$$\%C/12.01 = 44m + 5n \quad (1)$$

$$\%H/1.00 = 50m + 8n \quad (2)$$

$$\text{mol \% of BPB unit} = m/m + n \quad (3)$$

$$\text{mol \% of MAA unit} = n/m + n \quad (4)$$

Due to the highly ionic nature of all of the polymers, a GPC measurement for molecular weight could not be accomplished using our existing GPC system with THF eluent. However, the desolution behavior in THF or dimethylformamide (DMF) solvent revealed that all polymers have reasonably high molecular weights. Moreover, flexible films can easily be prepared from the polymer solution in DMF.

Thermal Behavior. All polymers exhibit good thermal stability, both in an inert atmosphere and in the presence of oxygen. All of the samples were heated at a steady rate as weight loss was monitored. The polymers, which are ionic in nature, may lose weight as they decompose. TGA studies (Figure 3) under nitrogen showed that polymer **CP2** was the most stable and could withstand heating up to a temperature of about 260 °C. [The decomposition temperature, T_d, was recorded as that point at which 5% weight loss occurred at a heating rate of 20 °C/min.] The melting temperatures T_m and T_d change systematically with their composition for all polymers. Both T_m and T_d increased with an increase in the MMA units in the polymeric systems. T_m was determined by DSC measurement at a heating rate of 10 °C/min.

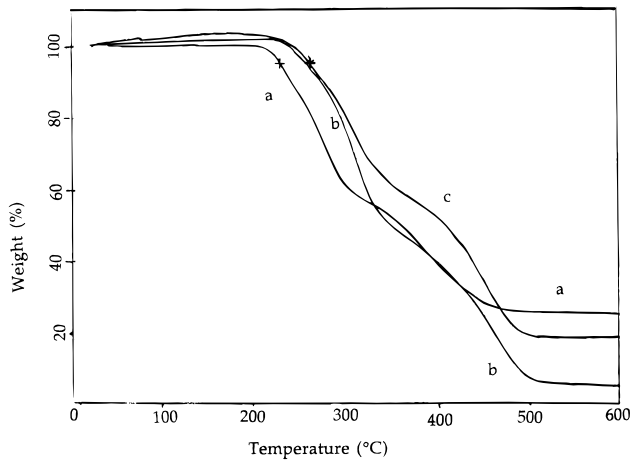


Figure 3. TGA diagram of (a) **H1**, (b) **CP1**, and (c) **CP2**.

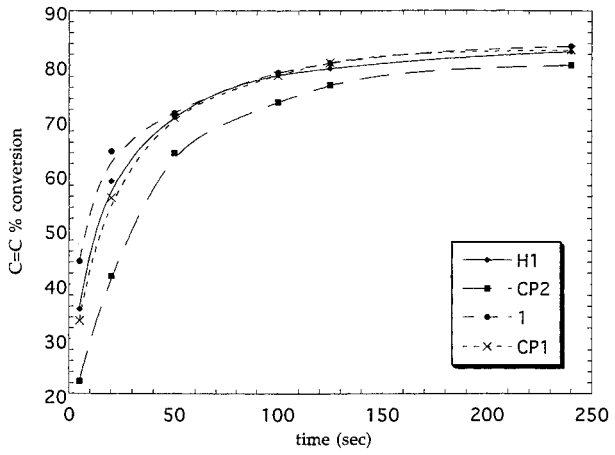


Figure 4. Photoinitiated polymerization of diacrylate monomer using various photoinitiators (3.06×10^{-5} mol of benzophenone borate chromophore) in the presence of air.

Table 2. Thermal Properties of Synthesized Polymers

sample	T_g (°C)	T_m (°C)	T_d (°C)
H1		115	229
CP1	90	121	259
CP2	95	128	264

No glass transition temperature, T_g, was observed for polymer **H1**. This is not surprising because of high crystallinity due to the ionic nature of the polymer. However, incorporation of MMA units in the copolymers decreased the crystallinity, and DSC studies revealed the T_g above 90 °C for copolymers. The T_g, T_m, and T_d values for all polymers are summarized in Table 2. The results indicate that the compositions of the polymers dramatically affect the thermal properties.

Photoinitiation Activity. The UV spectra of each of the polymers showed an absorption at 350 nm due to the benzophenone chromophore. This clearly suggests that the polymeric nature does not appear to affect general photophysical properties such as absorption and emission of the benzophenone moiety. All photoinitiation experiments were carried out using the same monomer, diethylene glycol diacrylate, and employing identical irradiation intensities and times of exposure. Figure 4 shows the efficiency as photoinitiators of the homo- and copolymers when compared to model compound **1** using identical concentrations of benzophenone borate chromophores (3.06×10^{-5} mol with respect to the total weight of the photoinitiator). Each initiator was compared under conditions of dilute chromophore concentration since we were unable to dissolve **CP2** in monomer at high concentrations. The highest photoactivity in terms of C=C bond conversion was observed for model compound **1** when compared to **H1** and the **CP**s. There was almost no induction period. This result suggests that low local concentrations of the resulting radicals favor the initiation process rather than radical recombination. It can be noted from Figure 4 that essentially the same kinetic profiles were found for polymer **H1** and copolymer **CP1,** although Figure 5 shows significantly slower results with **CP1** than those with **H1**. Structural changes from homo- to copolymer with methyl methacrylate (1:1) appeared to have little effect on either the cure speed and the extent of cure, especially at low concentration. Further increases in the methyl methacrylate units in copolymer **CP2** lead to a lower activity with a significant induction period. This induction period is probably attributed to mobility restrictions of the reactive sites in the polymeric system. The radicals that generate upon irradiation need to travel from the spaghetti-like polymeric coiling cage to the reactive monomeric site, and this is obviously slow.

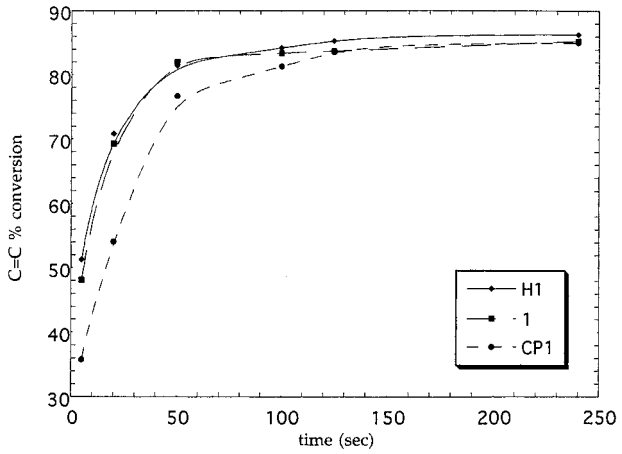


Figure 5. Photoinitiated polymerization of diacrylate monomer using various photoinitiators (6.12×10^{-5} mol of benzophenone borate chromophore) in the presence of air.

Table 3. UV Curing (Percent of Double Bond Conversion) of Diethylene Glycol Diacrylate Using Different Concentration of Photoinitiators

exposure time[a] (s)	$(3.06 \times 10^{-5})^b$				$(6.12 \times 10^{-5})^b$			$(1.22 \times 10^{-4})^b$	
	1	H1	CP1	CP2	1	H1	CP1	1	H1
05	50.0	35.5	33.4	22.3	44.2	51.3	35.8	33.2	79.2
20	64.3	58.8	55.8	41.5	67.2	70.8	54.1	71.6	86.9
50	74.5	70.7	70.5	64.0	76.2	81.4	76.7	82.8	88.8
100	82.2	78.3	78.2	73.3	79.3	84.2	81.3	87.4	91.4
180	84.2	82.5	81.2	78.7	81.8	86.2	84.3	89.9	92.4
240	84.5	82.5	82.8	80.0	82.1	86.3	85.0	90.1	92.7

[a] Accumulative time. [b] Mole concentration of benzophenone borate moieties.

At higher borate chromophore concentration, the kinetic behavior changes for the polymeric initiators, including model compound **1**. The conversion of vinyl groups in the film at different photoinitiator concentrations is shown in Table 3. The degree of conversion increased to a maximum 93% for **H1**, whereas compound **1** reached 90% at the same chromophore concentration (Figure 6). This was interpreted as due to an increased radical combination at higher concentration in **1**, resulting in the termination of the polymerization instead of chain propagation. In the case of **H1**, coupling between radicals became restricted without appreciably affecting their capability to initiate the

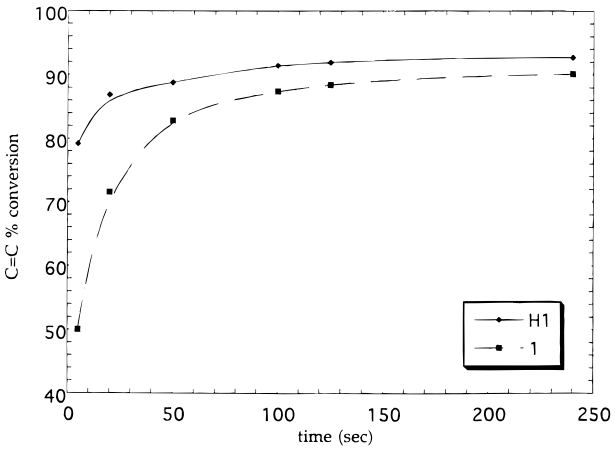
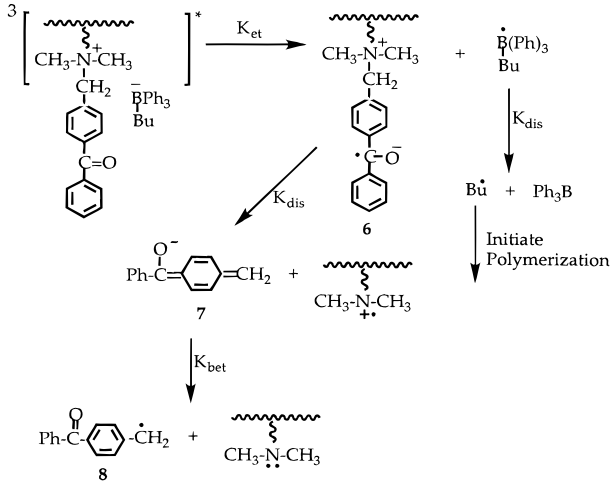


Figure 6. Photoinitiated polymerization of diacrylate monomer using model compound **1** and **H1** (1.22×10^{-4} mol of benzophenone borate chromophore) in the presence of air.

Scheme 5



polymerization of unsaturated monomers. This is likely due to steric hindrance.

When the efficiency of **H1** was compared with copolymers **CP1** (6.12×10^{-5} mol chromophore concentration) and **CP2** (3.06×10^{-5} mol) using the same irradiation time (Table 3), the C=C bond conversion was markedly decreased with an increase in the methyl methacrylate units in the polymeric main chains. This could be interpreted in terms of energy migration and effective collision between two or more chromophore groups.[16,17] With an increase in the number of methyl methacrylate units in the copolymer, an increase in the "mean distance" between two side chain chromophores results. Therefore, the electron transfer process becomes slow due to the low probability of intermolecular collision between two benzophenone borate groups according to Hirayama's "critical transfer distance" theory.[18]

Conclusion

The results strongly suggest that the main contribution to the photoactivity of all photoinitiators containing borate salts derives from efficient formation of butyl radicals by irradiation at 350 nm. The mechanism is similar to that proposed by us[7,19] and is shown in Scheme 5. Initial electron transfer from the borate anion to the benzophenone triplet state gives **6** and boranyl radicals, both of which dissociate rapidly. Radical **6** dissociates to give **7** and the amino cation radical followed by a second electron transfer to give free amine and stable radical **8**. On the other hand, dissociation of the boranyl radical within less than a picosecond[19] gives the butyl radical, which eventually initiates radical polymerization due to its extreme reactivity. The electron transfer process may be an intra- and intermolecular process, depending on the polarity of solvent. However, in our polymeric systems, the photoreactive borate moieties may come very close to each other due to coiling of the polymeric chain. Therefore, intra- and intermolecular electron transfer processes are likely to occur. Moreover, the increased photoinitiation activity of the polymers with increasing concentration against the model compound may be indicative of the major role of intermolecular electron transfer with respect to the intramolecular one.

In conclusion, these polymeric systems are exceptionally stable compared to most of conventional small molecule photoinitiators. These crystalline polymers are insensitive to air and moisture and show better photoinitiating activities in comparison with typical photoinitiator benzophenone in the polymerization of vinylic double bonds under identical conditions. This is likely important in the further design and synthesis of polymeric photoinitiators for UV-curing applications.

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References and Notes

(1) Contribution No. 289 from the Center for Photochemical Sciences.
(2) Carlini, C.; Angiolini, L. *Advances in Polymer Sciences*; Springer: Berlin, 1995; Vol. 123, p 127.
(3) Davidson, R. S. *J. Photochem. Photobiol. A: Chem.* **1993**, *69*, 263.
(4) Zweifel, H.; Berger, J.; Kvita, V; Roth, M. Eur. Pat. Appl. 0,033,721, 1985.
(5) LiBassi, G.; Nicora, C.; Cadona, L.; Carlini, C. Eur. Pat. Appl. 0,161,463, 1985.
(6) Angiolini, L.; Caretti, D.; Covelli, E.; Carlini, C. *J. Appl. Polym. Sci.* **1995**, *55*, 1477.
(7) Hassoon, S.; Sarker, A.; Rodgers, M. A. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11369.
(8) Sarker, A. M.; Polykarpov, A. Y.; Neckers, D. C.; deRaaff, A. M., *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 2817.
(9) Itoh, T.; Hall, H. K. *Macromolecules* **1990**, *23*, 4879.
(10) Adair, P. C.; Moore, M. J. U. S. Pat. US4,751,102, 1988.
(11) Sarker, A. M.; Mejiritski, A.; Wheaton, B. R.; Neckers, D. C. *Macromolecules*, submitted for publication.
(12) Angiolini, L.; Caretti, D.; Carlini, C.; Lelli, N. *Polym. Adv. Technol.* **1993**, *4*, 375.
(13) Hoyle, C. E.; Kim, K.-J. *J. Appl. Polym. Sci.* **1987**, *33*, 2985.
(14) Bradly, G.; Davidson, R. S. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 528.
(15) Revilla, J.; Delair, T.; Pichot, C.; Gallot, B. *Polymer* **1996**, *37*, 687.
(16) Kamachi, M.; Kikuta, Y; Nozakura, S. *Polym. J.* **1979**, *11*, 273.
(17) David, C.; Naegelen, V.; Piret, W.; Geuskens, G. *Eur. Polym. J.* **1975**, *11*, 569.
(18) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978.
(19) Hassoon, S.; Sarker, A.; Polykarpov, A. Y.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem.* **1996**, *100*, 12386.

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